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Equal Footing of Thermal Expansion and Electron-Phonon Interaction in the Temperature Dependence of Lead Halide Perovskite Band Gaps

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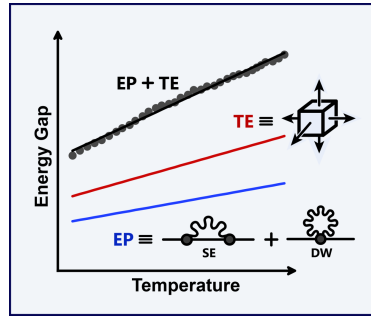
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Abstract

Lead halide perovskites, which are causing a paradigm shift in photovoltaics, exhibit an atypical temperature dependence of the fundamental gap: it decreases in energy with decreasing temperature. Reports ascribe such a behavior to a strong electron-phonon renormalization

of the gap, neglecting contributions from thermal expansion. However, high pressure experiments performed on the archetypal perovskite MAPbI_3 (MA stands for methylammonium) yield a negative pressure coefficient for the gap of the tetragonal room-temperature phase, which speaks against the assumption of negligible thermal expansion effects. Here we show that for MAPbI_3 the temperature-induced gap renormalization due to electron-phonon interaction can only account for about 40% of the total energy shift, thus implying thermal expansion to be more if not as important as electron-phonon coupling. Furthermore, this result possesses general validity, holding also for the tetragonal or cubic phase, stable at ambient conditions, of most halide perovskite counterparts.

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Hybrid lead halide perovskites of the type APbX_3 with organic A-site cation and halide substitution on the X site are the focus of attention of photovoltaic research and to a lesser extent as light emitters. These materials, which can be cost-effectively deposited from solution, experienced a rash improvement in solar-energy conversion efficiency, recently reaching a remarkable value of 23.7%.¹ For a solar cell as well as for a light emitting device, the band gap and its temperature dependence are fundamental properties of the active material. A peculiarity of the tetragonal and cubic phases of hybrid lead halide perovskites, which are stable at ambient conditions, is that they

exhibit an *atypical* dependence on temperature of the fundamental direct gap: it decreases in energy with decreasing temperature. This temperature dependence of the gap is almost ubiquitous in halide perovskites, as it can be found, for example, in MAPbI₃,^{2–6} MAPbBr₃,^{4,5,7} MAPbCl₃,⁸ FAPbI₃,⁵ FAPbBr₃,^{4,5} FA_xMA_{1–x}PbI₃,⁹ CsPbI₃,¹⁰ CsPbBr₃,^{10,11} MASnI₃¹² and CsSnI₃.¹³ By atypical it is meant opposite to the temperature behavior of the gaps exhibited by most of covalent bonded semiconductors, for which the gap increases with decreasing temperature (see, for instance, Refs.^{14–18} and references therein).

The theoretical framework for describing the variation of band gaps with temperature was set by V. Heine and P.B. Allen¹⁹ and further developed by M. Cardona and coworkers using the empirical pseudopotential method at an early stage^{14,15,17,20} and ab-initio techniques afterwards.^{18,21,23} The changes of the semiconductor band structure with temperature arise essentially from the effect of thermal expansion (TE) due to the anharmonicity of the crystal potential and from electron-phonon interaction. The renormalization of the band energies due to electron-phonon coupling, when considered to second order in the atomic displacements, consists of two terms: The Debye-Waller (DW) and the self-energy (SE) corrections. Usually, for the direct gaps of most semiconductors both terms cause a reduction with increasing temperature. The decrease caused by thermal expansion is mainly due to a positive hydrostatic pressure coefficient of the gaps, whereas the gap reduction arising from electron-phonon interaction is proportional to the Bose-Einstein phonon occupation number. There are, however, exceptions to the mentioned rule. The first reported material which appeared to show an abnormal temperature dependence of the fundamental gap was CuCl, which exhibits a slight sublinear increase of the gap with increasing temperature.²¹ Other cuprous halides²² and several silver chalcopyrites like AgGaS₂ and AgGaSe₂ also display abnormal behavior but at low temperatures.²³ A common characteristic of copper halides and silver chalcopyrites is that the pressure coefficient of the gap is very small, such that the thermal

expansion contribution to the gap renormalization becomes almost irrelevant. As a consequence, in these cases, the temperature dependence of the gap is mainly determined by electron-phonon interaction. As far as halide perovskites are concerned, thermal expansion effects were indeed considered at an early stage²⁴ and even taken as the only cause of band gap renormalization.¹³ However, probably misled by the copper halide results, researchers adopted lately the point of view of interpreting the atypical temperature dependent renormalization of the fundamental gap of lead halide perovskites exclusively as due to a particularly strong electron-phonon coupling.^{7,10} Recent results from first principle calculations also seem to indicate that lattice expansion has negligible effects on the band structure of MAPbI₃ in comparison to the electron-phonon coupling.²⁵ Here we show this is not the case.

In this Letter, we demonstrate that the role of the electron-phonon interaction in the temperature-induced renormalization of the gap of lead halide perovskites has been widely overestimated. Using available data for the hydrostatic pressure coefficient of the gap, we show for the archetypal perovskite compound MAPbI₃ that the thermal expansion contribution is the leading term in the temperature dependence of the direct gap, whereas electron-phonon interaction effects accounts for ca. 40% of the total energy shift. Moreover, we provide arguments in favor of an interpretation of the sign and magnitude of the electron-phonon renormalization terms, which holds also for other halide perovskites. Based on the results of previous empirical pseudopotential calculations, we infer that the electron-phonon coupling affects electronic states in different ways, depending on their bonding/antibonding and atomic orbital character.

The MAPbI₃ samples used for the high pressure experiments are high quality single crystals grown by the space-confined on-substrate fabrication method, as reported elsewhere,²⁶ having a suitable final thickness of ca. 30 μm . Otherwise, for the experiments as a function of temperature we used large and thick single crystals of about $2 \times 2 \times 1 \text{ mm}^3$ synthesized from aqueous solution

by similar procedure.²⁷ The high-pressure photoluminescence (PL) measurements were performed at room temperature employing a gasketed diamond anvil cell (DAC) with anhydrous propanol as pressure transmitting medium,²⁶ whereas the temperature dependent PL measurements were carried out in vacuum using a gas-flow cryostat.⁹ The PL spectra were excited with the 633 nm line of a He-Ne laser using a very low incident light power of ca. $1 \mu\text{W}$ (a power density below 15 W/cm^2) to avoid photo-degradation of the samples. Spectra were collected using a $20\times$ long working distance objective with $\text{NA}=0.35$ and dispersed with a high-resolution LabRam HR800 grating spectrometer equipped with a charge-coupled device detector. PL spectra were corrected for the spectral response of the spectrometer by normalizing each spectrum using the detector and the 600-grooves/mm grating characteristics.

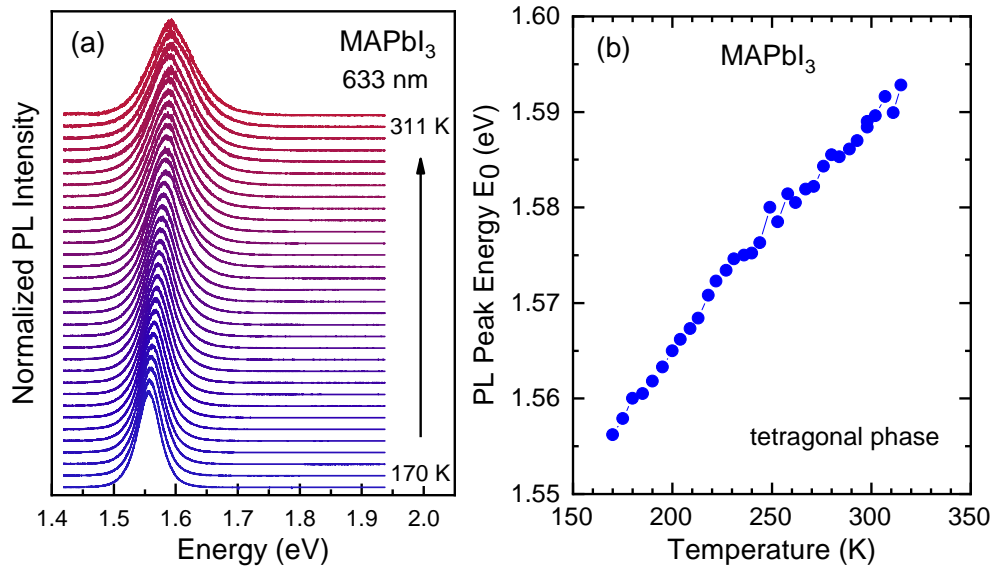


Figure 1: (a) PL spectra of MAPbI₃ measured at different temperatures in the range of stability of the tetragonal phase (ca. 170 to 311 K) using the red line (633 nm) for excitation. The spectra were normalized to their maximum intensity and plotted with a vertical shift for increasing temperature. (b) Plot of the temperature dependence of the maximum peak position E_0 of the spectra displayed in part (a).

Figure 1a shows the evolution of the PL spectra with temperature in the stability range of the

tetragonal phase of MAPbI₃. All spectra were normalized to its absolute maximum intensity and vertically offset for clarity. The main PL peak exhibits a gradual redshift and sharpening with decreasing temperature. To analyze the PL spectra of MAPbI₃ we used a Gaussian-Lorentzian cross-product function for describing the main peak which is ascribed to free-exciton recombination.²⁶ The values of the fitting parameter corresponding to the energy E_0 of the PL peak maximum are plotted as a function of temperature in Fig. 1b. Although we cannot tell the absolute values of bandgap and/or exciton binding energy from the lineshape fits, the shift of the PL peak energy E_0 with temperature (or pressure) is to a large extent dictated by the shift of the gap which for MAPbI₃ exhibits a fairly linear decrease with decreasing temperature.

As mentioned before, the derivative of the gap over temperature contains two terms; one accounts for thermal expansion effects (TE) and the other corresponds to the renormalization directly caused by electron-phonon interaction (EP), which includes the Debye-Waller and self-energy corrections:^{14,15,21}

$$\frac{dE_g}{dT} = \left[\frac{\partial E_g}{\partial T} \right]_{TE} + \left[\frac{\partial E_g}{\partial T} \right]_{EP}. \quad (1)$$

The effect on the gap due to the contraction of the lattice with decreasing temperature is intimately related to the response of the electronic band structure upon application of external hydrostatic pressure. It thus holds^{14,15,18}

$$\left[\frac{\partial E_g}{\partial T} \right]_{TE} = -\alpha_V \cdot B_0 \cdot \frac{dE_g}{dP}, \quad (2)$$

where $-\alpha_V$ is the volumetric expansion coefficient, B_0 is the bulk modulus, i.e. the inverse of the compressibility, and $\frac{dE_g}{dP}$ is the pressure coefficient of the gap, which can be determined from high pressure experiments. The last two factors depend only weakly on temperature. As shown in the Supplementary Information, the strongest temperature variation comes from α_V (also including zero-point vibrations¹⁸). At room temperature α_V is positive and the sign of Eq. (2) for the thermal

expansion contribution is determined by the sign of the pressure coefficient. For most semiconductor direct gaps $\frac{dE_g}{dP}$ is positive as well. Hence, thermal expansion causes a gap reduction. The lead halide perovskites are an exception. Figure 2 shows the variation with pressure of the energy position of the PL peak measured in MAPbI₃ single crystals with the DAC in the short stability range of the tetragonal phase. A linear fit to the data points (dot-dashed line) yields an unusually large but negative pressure coefficient, as indicated. The negative sign of $\frac{dE_g}{dP}$ arises from the inverted atomic orbital character of the states at the top and bottom of the valence and conduction band of MAPbI₃, respectively, as explained elsewhere.²⁶ This implies that for MAPbI₃ the expansion of the lattice with increasing temperature leads to a gradual opening of the gap, as displayed in Fig. 1b. The magnitude of this effect will be discussed later together with the gap renormalization due to electron-phonon interaction.

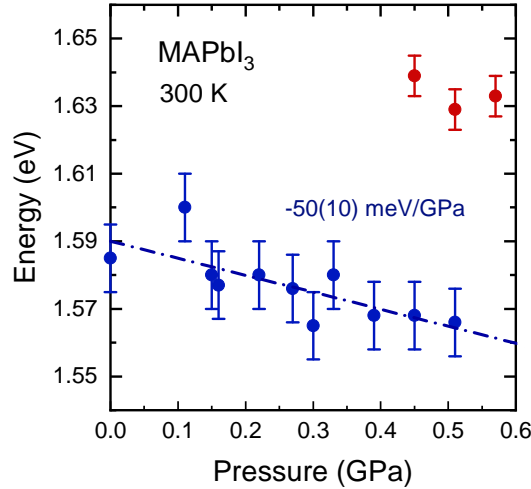


Figure 2: The energy E_0 of the PL peak maximum (blue symbols) plotted as a function of pressure in the stability range of the tetragonal phase of MAPbI₃. The dot-dashed line represents a fit to the data points using a linear function (its slope is indicated). The red symbols correspond to PL emission from regions of the sample which had already underwent the phase transition into the high pressure cubic phase (see Ref.²⁶ for details).

Gopalan *et al.*¹⁵ derived an expression for the shift and broadening induced by temperature,

through electron-phonon interaction, of any electronic state $E_{n\mathbf{k}}$ with band index n and wavevector \mathbf{k} , for which all phonon modes of the branch j , wavevector \mathbf{q} and frequency $\omega_{j\mathbf{q}}$ contribute:

$$\Delta E_{n\mathbf{k}}(T) = \sum_{j\mathbf{q}} \frac{\partial E_{n\mathbf{k}}}{\partial n_{j\mathbf{q}}} \left(n_{j\mathbf{q}}(T) + \frac{1}{2} \right), \quad (3)$$

where $n_{j\mathbf{q}} = \left(e^{\beta \hbar \omega_{j\mathbf{q}}} - 1 \right)^{-1}$ is the Bose-Einstein phonon occupation factor with $\beta = \frac{1}{k_B T}$. The real part of the complex interaction coefficients $\frac{\partial E_{n\mathbf{k}}}{\partial n_{j\mathbf{q}}}$ contribute to the energy shift of the bands and contain both the DW and SE parts, whereas the imaginary part leads to a lifetime broadening of the electronic states. Obviously, the sign of the renormalization of a gap is thus determined by the difference in magnitude and sign of the respective energy shift of valence and conduction band.

By invoking energy conservation, the summation in Eq. (3) transforms into an integral over the phonon frequencies:¹⁵

$$\begin{aligned} \Delta E_{n\mathbf{k}}(T) &= \int_0^\infty d\omega \cdot g^2 F(n, \mathbf{k}, \omega) \cdot \left(n_{j\mathbf{q}}(T) + \frac{1}{2} \right) \\ g^2 F(n, \mathbf{k}, \omega) &= \sum_{j\mathbf{q}} \frac{\partial E_{n\mathbf{k}}}{\partial n_{j\mathbf{q}}} \delta(\omega - \omega_{j\mathbf{q}}). \end{aligned} \quad (4)$$

The function $g^2 F(n, \mathbf{k}, \omega)$ is the so-called electron-phonon spectral function and is essentially the phonon density of states (DOS) appropriately weighted by electron-phonon matrix elements. As such, the spectral function is temperature independent, which means that the temperature dependence of the electron-phonon contribution to the gap shift arises solely from the Bose-Einstein occupation factor $n_{j\mathbf{q}}(T)$.

This is an important result because Eqs. (3) and (4) clearly indicate that the main contributions to the electron-phonon renormalization of the gap arise from peaks in the phonon density of states. In fact, this is at the origin of the Einstein-oscillator model introduced by Cardona and coworkers,

^{21–23} which approximate the $\frac{\partial E_{nk}}{\partial n_{jq}}$ coefficients by effective electron-phonon interaction parameters A_i for phonons with average frequency ω_i , inferred from the peaks in the phonon DOS. The EP correction to the gap then reads

$$[\Delta E_g(T)]_{EP} = \sum_i A_i \cdot \left(n_B(\omega_i, T) + \frac{1}{2} \right), \quad (5)$$

where n_B again stands for the Bose-Einstein factor. In special cases of materials with two atoms per unit cell with markedly different masses like the cuprous halides,^{21,22} it is allowed to use a two-oscillator model with a modified effective EP coefficient which explicitly accounts for its dependence on the average phonon frequency and atomic specie mass ($A_i \rightarrow \frac{A'_i}{\omega_i \cdot M_i}$). This is justified because the phonon DOS exhibits two peaks, one at the average frequency of the acoustic phonon branches at the Brillouin zone edges, corresponding to vibrations of the heavier mass specie, and another oscillator accounting for the optical phonon contribution, corresponding to vibrations of the lighter mass atomic specie. For exactly the same reason each of the two oscillators is identified with the contribution from acoustic and optical phonons to the electron-phonon renormalization. We point out that this model cannot be simply transferred to the case of the halide perovskites,^{7,10} because perovskites have many atoms per unit cell and the vibrations cannot be classified as lead only or halide only. In fact, an inspection of the phonon DOS for the three methylammonium lead halide compounds²⁸ indicates that the DOS exhibits up to four well-defined peaks or bands, not two, with partial intermixing of optical and acoustical branches.

In this respect, we show here that the electron-phonon renormalization can be well accounted for using a single Einstein oscillator with a *positive* effective coefficient $A_{eff.}$, so as to reproduce the linear decrease of the gap with decreasing temperature of MAPbI₃. Since we do not know the absolute magnitude of the gap renormalization at room temperature (or at any other temperature), we decided to circumvent this handicap by evaluating instead the derivative with respect

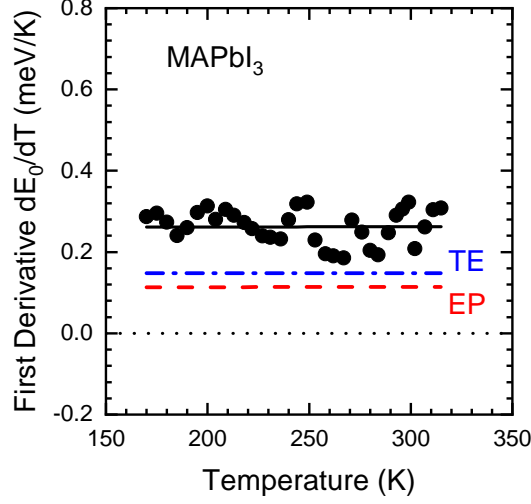


Figure 3: The first derivative of the PL peak energy E_0 with respect to temperature (closed black symbols), numerically calculated from the data of Fig. 1b. The solid black line represents a fit to the data points, corresponding to the sum of the contribution of thermal expansion (blue dot-dashed curve) and electron-phonon interaction (red dashed curve). See text for details.

to temperature of the gap renormalization. The closed black symbols in Fig. 3 represent the first derivative over temperature of the bandgap, numerically calculated point-by-point from the data set of E_0 versus T shown in Fig. 1b. Despite the dispersion of the values, in the temperature range of stability of the tetragonal phase of MAPbI₃, the first derivative of the gap over temperature is, as expected, essentially constant. The contribution from thermal expansion can be directly obtained from Eq. (2), using the values of $\alpha_V = 1.57 \times 10^{-4} \text{ K}^{-1}$ ²⁹ and $B_0 = 18.8 \text{ GPa}$ ³⁰ from the literature and the linear pressure coefficient determined by us from high pressure experiments, indicated in Fig. 2. The result is the constant contribution represented by the blue dot-dashed line in Fig. 3. In order to calculate the contribution from electron-phonon interaction, we have derived Eq. (5) with respect to temperature, considering a single oscillator with coupling constant $A_{eff.}$ and oscillator frequency $\omega_{eff.}$:

$$\left[\frac{\partial E_g}{\partial T} \right]_{EP} = \frac{A_{eff.}}{4T} \cdot \frac{\hbar \omega_{eff.}}{k_B T} \cdot \frac{1}{\sinh^2 \left(\frac{\hbar \omega_{eff.}}{2k_B T} \right)}. \quad (6)$$

This function together with the constant contribution from TE given by Eq. (2) were fitted to the data points of Fig. 3 using only the electron-phonon coupling constant and the average phonon frequency as adjustable parameters. The resulting values for these parameters are: $A_{eff.} = 8.0(8)$ meV and $\hbar\omega_{eff.} = 5.8(6)$ meV, where the numbers in parentheses are the error bars (uncertainty of the last digits). The solid black curve and the dashed red curve in Fig. 3 represent the resulting total rate of gap renormalization per Kelvin and the EP contribution to it, respectively. We emphasize that without further information apart from the data of Fig. 1b the only way to ensure uniqueness of the fitting results is to use one Einstein oscillator. Addition of further oscillators would just introduce strong correlations between oscillators parameters, leading to multi-valued solutions. In summary, at 300 K we obtain from the fitting results a total renormalization rate of 0.26(5) meV/K, corresponding to the sum of the contribution from thermal expansion (0.15(5) meV/K) and that from electron-phonon interaction (0.11(5) meV/K). This is a clear indication that thermal expansion effects ($\sim 60\%$), rather than being negligible,^{7,10,25} are even more important than electron-phonon coupling effects ($\sim 40\%$). We show below that this situation also holds for most, if not all, lead halide perovskites investigated so far.

By accounting for the thermal expansion effects, we obtain within the Einstein-oscillator model a value of ca. 6 meV for effective phonon frequency involved in the gap renormalization, which is in excellent agreement with the frequency of 1 THz (approx. 4 meV) of the specific phonon mode which strongly couples to the gap in THz transient transmission experiments⁶ and with the frequency of 4.2(8) meV of the phonons leading to exciton broadening,³¹ both in MAPbI₃, although the latter holds for the orthorhombic phase. In contrast, if the two-oscillator model is applied without thermal expansion consideration, unrealistically large average phonon frequencies for the optical branches of approx. 16 meV⁷ or even 40 to 50 meV¹⁰ are found for the best fit to the gap-versus-temperature data. We recall that the maximum cutoff frequency of the phonon modes

of the inorganic cages of lead halide perovskites is 200 cm^{-1} (ca. 25 meV)³² but the most intense Raman modes have frequencies below 100 cm^{-1} (ca. 12.5 meV).²⁸ For comparison we show in the Supporting Information results from a literature survey containing a comprehensive list of available band-gap pressure and temperature coefficients for different halide perovskite materials.

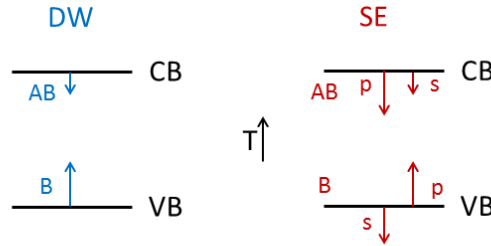


Figure 4: Sketch of the sign and magnitude (arrows) of the Debye-Waller (DW) and self-energy (SE) contributions to the electron-phonon renormalization of valence and conduction band states of sp^3 bonded semiconductors, depending on the bonding (B) or antibonding (AB) and atomic orbital character (s or p) of the involved states for the case of increasing temperature (T).

The calculation by ab-initio methods of the magnitude of the electron-phonon interaction in materials like the hybrid halide perovskites, characterized by soft and strongly anharmonic vibrational modes, constitutes a real challenge.^{5,24,33,34} Despite their relevance, we prefer to make use of the semiempirical pseudopotential calculations that provided a detailed, though qualitative, picture of the electron-phonon interaction in covalent, sp^3 -bonded semiconductors^{14,15,17,20} (for further details see the Supplementary Information). The Debye-Waller correction represents two-phonon processes for which the lattice vibrations perturb the electronic band structure in the same way as in the case of x-ray diffraction patterns, i.e., by smearing the pseudopotential *structure factor*. In this sense, the DW correction mainly depends on the spatial distribution of the electronic charge around the lattice atoms. As illustrated in the sketch of Fig. 4, valence band states with mostly bonding character increase in energy with increasing temperature, whereas the antibonding conduction band states slightly decrease in energy. Hence, the DW term always cause a gap

reduction with increasing temperature for sp^3 -bonded semiconductors. In contrast, the sign and magnitude of the self-energy term would depend on how the pseudopotential *form factors* react to the different phonon eigenvectors corresponding to the modes leading to the peaks in the phonon DOS. It turns out that the acoustic-phonon SE contribution almost cancels out the DW correction,¹⁵ which implies that for sp^3 bonding only optical phonon contribute to the gap renormalization. The remaining SE interaction matrix elements are large and positive for p -like and moderate but negative for s -like bonding valence-band states, whereas for antibonding conduction-band states the SE interaction parameters are negative for s and p -like states but larger for the latter (see Fig. 4). As a consequence a single Einstein oscillator with a negative coupling constant A_{eff} provides a good description of the gap reduction induced by an increase in temperature in conventional semiconductors.

A common feature of the materials showing an abnormal temperature dependence of their gap, like certain cuprous halide^{21,22} and Ag chalcopyrite²³ compounds, is the presence of d -states in the valence band. The Cu $3d$ and Ag $4d$ -like valence electrons hybridize with the usual p -like counterparts, reverting the sign of the electron-phonon interaction and so leading to a strong downshift of the valence band with increasing temperature. The d -states hybridization also has important consequences for the pressure coefficient of the gap,³⁵ which is largely reduced, because the AB d -states push up the top of the valence band with pressure at a similar pace than the upshift of the bottom of the conduction band. On the contrary, the unusual temperature-induced gap renormalization in lead halide perovskites possesses a different origin, since there is no hybridization with d -states whatsoever. It is the huge spin-orbit interaction which causes a so-called band inversion. Relativistic band-structure calculations^{36–38} for a pseudo-cubic phase of $MAPbI_3$ predict that for the direct gap at the R-point of the Brillouin zone the top of the valence band is predominantly composed by Pb $6s$ orbitals slightly hybridized with I $5p$ orbitals, whereas the bottom of the con-

duction band is formed by the split-off Pb 6*p*-orbitals. Hence, one expects the EP interaction to lead to a gap increase with increasing temperature (see Supplementary Information for details). This is supported by ultraviolet photoemission spectroscopy combined with optical gap measurements, which for MAPbI₃ show a stronger lowering of the valence band maximum with respect to the conduction band minimum, as temperature is raised.² We note that in tin halide perovskites,^{12,13} despite the weaker spin-orbit coupling as for lead-based compounds, a similar band inversion occurs, leading to a totally similar atomic orbital character of the electronic states at the conduction and valence band extrema^{40?, 41} like in MAPbI₃. Furthermore, such band inversion also explains the negative pressure coefficient observed in halide perovskites (see Supporting Information for a complete survey of literature data). The pressure coefficient determines the sign of the thermal expansion contribution, which thus adds up to the effects of electron-phonon interaction as far as the gap renormalization is concerned. Since all arguments presented here are valid for all halide perovskites crystallizing in the tetragonal and/or cubic phases, the same behavior of the gap with temperature, which is ubiquitous in this material system, has similar explanation.

In conclusion, we have shown that the importance of the electron-phonon interaction in the *ab-normal* temperature dependence of the fundamental gap of the tetragonal or cubic phases of halide perovskites has been widely overestimated in previous work. This was the result of totally neglecting the effects of thermal expansion. As a consequence, disproportionately large electron-phonon coupling constants and average phonon frequencies were needed to explain the variation of the gap with temperature in halide perovskites. Using MAPbI₃ as representative example, we showed that the thermal expansion effects can be readily quantified from the measured (also unusual) negative pressure coefficient of the gap. Our findings, which have general validity for halide perovskites, clearly indicate that thermal expansion has to be treated on equal footing with the electron-phonon interaction for the correct interpretation of temperature effects on their electronic structure. Given

the relevance of the electron-phonon interaction for a variety of physical phenomena apart from the temperature dependence of the gap (charge transport, exciton lifetimes, non-radiative relaxation processes, thermoelectric properties, etc.), its correct assessment is fundamental for further scientific and/or technological developments with halide perovskites.

Supporting Information

Contains details of the theoretical discussion, based on the empirical pseudopotential method, of the effects of thermal expansion and electron-phonon interaction on the renormalization of gaps with temperature for conventional semiconductors. It also contains a table with the gap pressure and temperature coefficients of the PL peak energy E_0 for the phase of different halide perovskites stable at ambient conditions and a plot showing the smoothing procedure of the data set E_0 -vs-temperature for the calculation of the first derivative.

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